

APPENDIX A
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Ladder-type and Blue Light-Emitting Polymer with Excellent Thermal Stability

FIELD OF THE INVENTION

The present invention relates to luminescent polymers, specifically ladder-type and blue light-emitting polymer with excellent thermal stability, which are prepared by polymerization of blue luminescent monomer or grafting blue luminescent monomer.

PRIOR ART

Polymers have been generally classified as insulators. Recently, conducting polymers such as polyaniline, polypyrrole and polythiophene have been developed, which provide conductivity as high as metal. These polymers have advantages over metal in aspects of light weight and processability.

Conjugated polymers with electrical and optical characteristics have been used for as anti-static materials, sensors, electrodes, transistors, light-emitting materials, solar cell, smart cards, electronic newspapers, and other display devices. Luminescence polymers have been extensively developed since the electroluminescence with poly(1,4-phenylenevinylene) was reported in Cambridge group in 1990 (Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. Nature 1990;347:539). Features of luminescence polymers are, in comparison with the inorganic materials, light weight, thin, self-luminescent, of low threshold voltage. These polymers also provide fast switching velocity, easy processability, low production cost, low dielectric constant, and most of all, the advantage of easy fabrication and controllable electrical and optical properties by the modification of their molecular structures, which allow these polymers to be promising

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candidates of light-emitting materials for information and communication technology of the next generation.

A blue luminescent polymer employs aromatic groups such as fluorene or spiro-fluorene such as conjugated polymers as described in U.S. Patent Nos. 5593788, 5597890, 5763636, and 5900327. In U.S. Patent No. 5998045, luminescent polymers were prepared by copolymerization of fluorene and anthracene. The copolymers-of fluorene and aromatic compounds (for example, carbazole) were reported in German Patent Nos. 198 46 766, 198 46 767, and 198 46 768. In U.S. Patent No. 6395410, electroluminescence devices were prepared with luminescent and transparent polymers.

Much effort is needed to achieve enhanced durability and brightness of the blue light-emitting polymers for their use in luminescent devices because of their poor thermal stability. Heat causes molecular movement and generates fine particles or coagulates. Heat generation increases in proportion to the period of working time of electroluminescence devices. The existing light-emitting polymers have the glass transition temperature at around 100 °C (Macromolecules; 1988; 31(4); 1099-1103) causing such problems.

SUMMARY OF THE INVENTION

Therefore, the inventors of the present invention intended to prepare the blue luminescent polymers with high melting point and with excellent thermal stability.

As a result, ladder-type blue light-emitting polymers that can solve the said problems are provided herein. These polymers can be formed by polymerization of blue luminescent monomers or grafting blue luminescent monomers.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1(a) is the conceptual picture of a conventional blue light-emitting polymer.

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Figure 1(b) is the conceptual picture of a ladder-type blue light-emitting polymer.

Figure 2 shows synthetic scheme of the ladder-type blue light-emitting polymer.

Figure 3 shows the UV-VIS spectra.

Figure 4 shows the photoluminescence spectra.

Figure 5 shows the TGA of P1.

Figure 6 shows the TGA of P2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides thermally stable and blue light-emitting polymers and the preparation therefor. Novel luminescent polymers with a ladder-type structure are described, which are thermally stable have a high glass transition temperature, above 400 °C; and high temperature of 5%-weight loss, above 450 °C, and are soluble in solvent for thin film applications. In these polymers, polystyrene, serving as backbone, is transparent in the visible region, increases compatibility with other polymers, inhibits molecular movement and increases thermal stability.

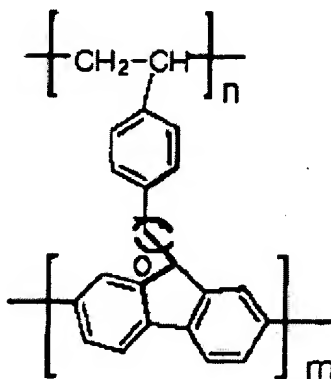
The conventional polyfluorene and polyaryl polymers have the structure of (a) as shown in Figure 1, and are movable at a higher temperature above 100 °C. The ladder-type polymers of the invention have a structural composition as shown in Figure 1 (b), where block A is light-emitting part and block B is polystyrene. Polystyrene has excellent optical properties, high thermal stability and inhibits molecular movement. The polystyrene block is readily dissolved in solvent, and allows easy fabrication.

Figures 1(a) and 1(b) show a conventional blue light-emitting polymer (a) and a ladder-type blue light-emitting polymer (b)

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The polymers as shown in Figure 1(b) can have different formula, which are described below:

The polymer of Figure 1(b), where **A** is selected from polyfluorene, polythiophene, polypyrrole, polycarbazole, polyphenylene, polyaniline, and polypyridine; **B** is selected from polystyrene, polypyrrol, polythiophene, polycarbonate, polyphenylene, polyaniline, polypyridine, and polycarbazole; *n* is an integer of 5 to 100; and *m* is an integer of 2 to 100. The blue light-emitting polymer can be represented by the following formula 1.

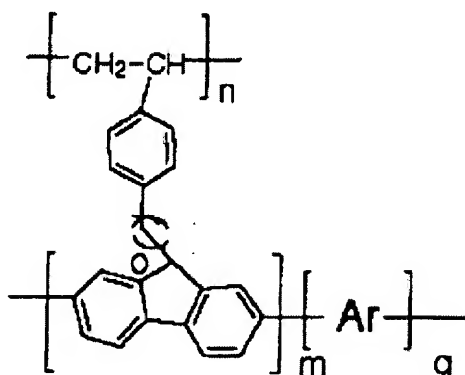


[Formula 1]

The polymer of Figure 1(b), where **A** is polyfluorene; **B** is polystyrene; *n* is an integer of 5 to 100; and *m* is an integer of 2 to 100.

And, the present invention provides the blue light-emitting polymers containing **Ar** compounds represented in the formula 2:

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[Formula 2]

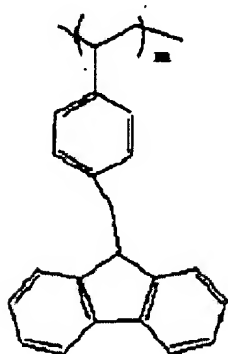
wherein **Ar** is an compound such as fluorene, fluorene derivatives, benzene, benzene derivatives, thiophene, thiophene derivatives, carbazole, carbazole derivatives, pyridine or pyridine derivatives; preferably, **B** is polystyrene with atactic or syndiotactic structure as shown in the formula 1 or 2.

The ladder-type blue light emitting polymers described above can be synthesized in various methods. Two exemplary synthetic schemes for the ladder-type blue light-emitting polymer are shown in Figure 2.

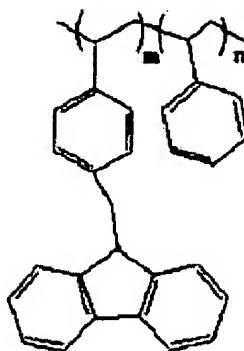
The first method comprises eliminating a hydrogen atom from C₉ position of fluorene or dibromofluorene using n-butyl lithium in tetrahydrofuran, grafting polyvinyl benzene chloride to it, and polymerizing aryl groups with nickel or iron catalyst (Figure 2, upper scheme).

The second method comprises substituting chloride atom of vinyl benzene chloride with fluorene, polymerizing styrene part, and polymerizing fluorene with nickel or iron catalyst. Other method includes polymerizing vinylfluorene, [formula 3], or copolymerizing styrene with vinylfluorene to make a polymer of [formula 4], and polymerizing fluorene groups (Figure 2, lower scheme).

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[Formula 3]



[Formula 4]

The following examples further illustrate the present invention in detail but do not limit the scope thereof.

Example 1: 9-Vinylbenzyl fluorene.

Fluorenyl lithium was prepared by reacting fluorene (10.0 mmol) with *t*-butyl lithium (1.7 M in *n*-pentane, 10.0 mmol) in THF (10 mL) at -78 °C for 2 hours. Fluorenyl lithium was slowly added to vinyl benzene chloride (10 mmol) in THF solution at -78 °C and reacted with stirring for 16 hours. Water (100 mL) and ether (100 mL) were added and stirred. Organic layer was extracted, dried and recrystallized to obtain needle shape and ivory solid.

¹H-NMR (200 MHz, CDCl₃): 7.77 (2H, d, Fu-H), 7.39-7.20 (10H, m, Fu-H, Bn-H), 6.80-6.66 (1H, q, Vy-H), 5.80-5.70 (1H, d, Vy-H), 5.27-5.21 (1H, d, Vy-H), 4.23 (1H, t, Fu-H), 3.10 (1H, d, Bz).

Example 2: Polyvinylbenzyl dibromofluorene

Under N₂ atmosphere, polyvinylbenzyl chloride (1.57 g, M_w 55,000) is dissolved in THF (20 mL). Dibromofluorene (3.24 g) was dissolved in THF (50 mL) and cooled to -78 °C. To this solution, 4 mL of *n*-butyl lithium (2.5 M, *n*-hexane solution) was added and the resulting solution

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was added slowly to the above polyvinyl benzene chloride solution. The mixture was stirred at room temperature for 6 hours and water was added. The product was extracted with ethyl ether (200 mL) and dried under vacuum. Obtained product was yellow solid. M_w : 272900. MWD: 5.71. UV-Vis (λ_{max} , THF): 298 nm.

Example 3: Polyvinylbenzyl fluorene

Under N_2 atmosphere, Polyvinylbenzyl chloride (1.57 g, M_w 55,000) was dissolved in THF (20 mL). Fluorene (1.67g) was dissolved in THF (50 mL) and cooled to -78 °C. To this solution added was 4 mL of n-butyl lithium (2.5 M, *n*-hexane solution). The resultant solution was added to the above polyvinyl benzyl chloride solution. The mixture was stirred for 6 hours at room temperature and water was added. The product was extracted with ethyl ether (200 mL) and dried under vacuum. Yellow solid was obtained.

M_w : 68160. MWD: 2.96. UV-Vis (λ_{max} , THF): 302 nm.

Example 4: Polyvinylbenzyl-polyfluorene (P1)

Under N_2 atmosphere, polyvinylbenzyl fluorene (1.57 g, M_w 55,000) and dihexylfluorene (3g) were dissolved in chloroform (20 mL). To the solution $FeCl_3$ (5g) was added and stirred for 4 hours at room temperature. To the mixture methanol was added and the produced precipitates were filtered. The obtained solids were dissolved in THF and the insoluble solids were discarded. The THF solution was dried under vacuum, and yellow solid was obtained.

M_w : 79040. MWD: 2.94. UV-Vis (λ_{max} , THF): 362 nm. PL (λ_{max} , THF): 542 nm. TGA (5%, °C): 475, Glass transition temperature(°C): 421.8.

Example 5: Polyvinylbenzyl-polyfluorene (P2)

Under N_2 atmosphere, polyvinyl benzyl dibromofluorene (1.57g, M_w 55,000) and dihexylfluorene(3g) were dissolved in chloroform(20 mL). To the solution $FeCl_3$ (5g) was

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added and stirred for 4 hours at room temperature. To the mixture methanol was added and the produced precipitates were filtered. The obtained solids were dissolved in THF and the insoluble solid was discarded. The THF solution was dried under vacuum, and yellow solid was obtained.

M_w : 132200. MWD: 2.07. UV-Vis (λ_{max} , THF): 362 nm. PL (λ_{max} , THF): 514 nm.
TGA (5%, °C): 448, Glass transition temperature (°C): 404.4.

Example 6: Polyvinylbenzyl-polyfluorene (P3)

Under N_2 atmosphere, polyvinyl benzyl dibromofluorene (1.57 g, M_w 55000) and dihexylfluorene (3 g) were dissolved in benzene (20 mL). To the solution $Pd(PPh_3)_4$ (5 g) was added and refluxed for 6 hours. To the mixture, methanol was added and the resultant precipitates were filtered. The obtained solid was dissolved in THF, and the insoluble solid was discarded. The THF solution was dried under vacuum, and yellow solids were obtained.

M_w : 159300. MWD: 4.34. UV-Vis (λ_{max} , THF): 330 nm. PL (λ_{max} , THF): 445 nm.

Example 7: Polyvinylbenzene-poly(fluorene-co-thiophene) (P4)

Under N_2 atmosphere, polyvinyl benzyl dibromofluorene (500 mg, M_w 55000) and 3-octylthiophene (2 g) were dissolved in chloroform (20 mL). To the solution $FeCl_3$ (2.5 g) was added and stirred for 4 hours at room temperature. To the mixture, methanol was added and the produced precipitate was filtered. The obtained solid was dissolved in THF, and the insoluble solid was discarded. The THF solution was dried under vacuum, and yellow solid was obtained.

M_w : 8911. MWD: 3.14. UV-Vis (λ_{max} , THF): 405 nm. PL (λ_{max} , THF): 544, 682 nm.
TGA (5%, °C): 280. Glass transition temperature (°C): 384.8

Example 8: Syndiotactic polyvinylbenzyl fluorene

Under N_2 atmosphere, 1-vinyl-4-(1-fluorenyl)methylbenzene (0.52g) was added into a flask and dissolved in toluene (20 mL). To the solution, 12.1 mmol of MAO (2.43 mg, 5 mL)

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was added slowly and stirred for 30 minutes. 10 mmol of CpTiCl_3 (2.19 mg) was dissolved in 1 mL of toluene and added slowly to the solution at room temperature. After addition, the mixture was stirred for one hour at room temperature and poured into a 200 mL of acidic methanol to obtain solid product. The product was washed with methanol, and dried under vacuum for several hours and 0.3 g of copolymer was obtained. M_w : 2500.

Example 9: Syndiotactic polyvinyl benzyl fluorene-co-styrene (**P5**)

Under N_2 atmosphere, styrene (2.1 g) and 1-vinyl-4-(1-fluorenyl)methylbenzene (0.52 g) were added into the flask and dissolved in toluene (20 mL). To the solution, 12.1 mmol of MAO (2.43 mg, 5mL) was added slowly and stirred for 30 minutes. 10 mmol of CpTiCl_3 (2.19 mg) was dissolved in 1mL of toluene and added slowly to the above solution at room temperature. After addition, the mixture was stirred for 2 hours at room temperature and poured into a 200 mL of acidic methanol to obtain solid product. The product was washed with methanol and dried under vacuum for several hours. 2.5 g of **P5** was obtained. M_w : 8,000.

Example 10: Syndiotactic polystyrene-polyfluorene (**P6**)

Under N_2 atmosphere, **P5** (500 mg, M_w 8000) was dissolved in chloroform (20 mL). To the solution, FeCl_3 (2.5 g) was added and stirred for 4 hours at room temperature. Methanol was added to the mixture and the precipitates were filtered. The solid precipitate was dissolved in THF and the insoluble solid was discarded. The THF solution was dried under vacuum, and yellow powder was obtained.

M_w : 4802. MWD: 2.42. UV-Vis (λ_{max} , THF): 353 nm, PL (λ_{max} , THF): 46 nm, TGA (5%, $^{\circ}\text{C}$): 232.8, Glass transition temperature ($^{\circ}\text{C}$): 413.5.

The polymers exhibited glass transitions (T_g), 422 $^{\circ}\text{C}$ for **P1**, 404 $^{\circ}\text{C}$ for **P2**, and 414 $^{\circ}\text{C}$ for **P3**, and no melting endotherms were found out. Syndiotacticity contributes the high glass

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temperature of **P3** in spite of low molecular weight. Thermal decomposition temperatures at 5%-weight loss (T_d), 475 °C for **P1**, 448 °C for **P2**, and 233 °C for **P3** were observed. The fluorescence peaks of **P1**, **P2**, **P3** were observed at 401 nm, 416 nm and 415 nm, respectively. For the emission spectrum of **P3**, no shoulder or peak regarding of aggregation of polyfluorene was observed.

Syndiotacticity, due to alternative configuration of fluorene, prevents a large Stoke's shift of the luminescence spectrum.

The polymers synthesized, as described above, have high thermal stability and a long life time maintaining the efficiency of light emission. To fabricate devices, the polymers can be coated on an electrode by spin-coating or ink-jetting. They can also increase the compatibility with the polymers of good optical properties (for example, polycarbonate, polymethylmethacrylate and polystyrene). The polymers can be copolymerized with aromatic compounds such as fluorene, benzene, thiophene, carbazole, pyridine, styrene and their respective derivatives.

The analytical instruments used are as following. Molecular weight was determined by GPC analysis (Viscotek Co.) using polystyrene standards and THF as solvent at 40 °C. JASCO V-570 and Varian Unit Inova 200 (200 MHz) were used to measure UV-visible and ^1H -NMR spectra, respectively. The thermal data of the ladder-polymers were obtained on nitrogen atmosphere at a rate of 20 °C/min by using Perkin-Elmer's TGC 7/7. Fluorescence spectra were obtained with SLM-AMINCO 4800 spectrofluorometer, in which Rhodamin was used as quantum counter.

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EFFECT OF THE INVENTION

A series of 2-dimensional ladder-type polyfluorenes was prepared by introducing atactic or syndiotactic polystyrene as the backbone. The ladder-type polyfluorenes have a high T_g more than 400 °C and excellent thermal stability. No remarkable aggregation of interchains was observed in the ladder-type polyfluorene having syndiotactic polystyrene as the backbone. Accordingly, the polymers can be utilized as blue light-emitting applications such as display devices, household electric appliances and cellular phones.